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Key Points:

- Groundwater fluctuations divide time series into hydrological seasons
- Dry season length increases production and accumulation of DOC in soils
- Runoff depletes the DOC stored in watershed soils during wet seasons

Supporting Information:

- Supporting Information S1

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Dry-season length and runoff control annual variability in stream DOC dynamics in a small, shallow groundwater-dominated agricultural watershed

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Abstract As a phenomenon integrating climate conditions and hydrological control of the connection between streams and terrestrial dissolved organic carbon (DOC) sources, groundwater dynamics control patterns of stream DOC characteristics (concentrations and fluxes). Influence of intra-annual variations in groundwater level, discharge and climatic factors on DOC concentrations and fluxes were assessed over 13 years at the headwater watershed of Kervidy-Naizin (5 km^2) in western France. Four seasonal periods were delineated within each year according to groundwater fluctuations (A: rewetting, B: high flow, C: recession, and D: drought). Annual and seasonal base flow versus stormflow DOC concentrations were defined based on daily hydrograph readings. High interannual variability of annual DOC fluxes (5.4–39.5 kg ha^{-1} yr^{-1}) indicates that several years of data are required to encompass variations in water flux to evaluate the actual DOC export capacity of a watershed. Interannual variability of mean annual DOC concentrations was much lower (4.9–7.5 mg C L^{-1}), with concentrations decreasing within each year from ca. 9.2 mg C L^{-1} in A to ca. 3.0 mg C L^{-1} in C. This indicates an intra-annual pattern of stream DOC concentrations controlled by DOC source characteristics and groundwater dynamics very similar across years. Partial least squares regressions combined with multiple linear regressions showed that the dry season characteristics (length and drawdown) determine the mean annual DOC concentration while annual runoff determines the annual flux. Antagonistic mechanisms of production-accumulation and dilution-depletion combined with an unlimited DOC supply from riparian wetland soils can mitigate the response of stream concentrations to global changes and climatic variations.

1. Introduction

The impacts of dissolved organic carbon (DOC) on aquatic ecosystems, either as a source of nutrients [*Anderson et al.*, 2002], a vector of pollutants [*Ravichandran*, 2004], or a regulator of light absorbance [*Reche et al.*, 1999], raise the need to understand its spatial and temporal dynamics. In headwater watersheds, stream DOC originates mainly from terrestrial sources [*Aitkenhead et al.*, 1999; *Billett et al.*, 2006] within which DOC mobility results from complex interactions between microbial and physicochemical processes [*Kaiser and Kalbitz*, 2012]. By affecting redox conditions, nutrient availability, decomposer activity, and groundwater levels, climate is an important control of both DOC production within the soil profile and DOC transfer to the stream [*Hornberger et al.*, 1994; *Marin-Spiotta et al.*, 2014].

The changes in groundwater level are known as a critical driver of DOC transfers at various scales of space and time due to their impact on water flow paths and thus on the connectivity between watershed soils and streams [e.g., *Laudon et al.*, 2011]. The presence of more riparian runoff than hillslope runoff explained higher DOC concentrations on the rising limb of the discharge hydrograph of storm events in watersheds of South Island, New Zealand [*McGlynn and McDonnell*, 2003]. *Morel et al.* [2009] used end-member mixing analysis to calculate the contribution of riparian soils to DOC export in the agricultural headwater watershed of Kevidy-Naizin in France. Between 64 and 86% of the DOC that entered the stream during storms originated from riparian wetland topsoil according to their calculations. While riparian wetland soils were identified as a near-infinite DOC source [*Morel et al.*, 2009], hillslope soils were also found to contribute to stream DOC export [*Inamdar and Mitchell*, 2006]. However, changes in dissolved organic matter (DOM) composition determined by isotopic and spectroscopic analyses revealed that DOM stored in the upland soils were supply-limited and thus was seasonally depleted after the rise of groundwater in these areas [*Lambert et al.*, 2013; *Sanderman et al.*, 2009; *van Verseveld et al.*, 2009]. *Lambert et al.* [2014] determined that upland DOC contribution decreased from ca. 30% of stream DOC flux at the beginning of the high-flow season to <10% later in the season in the Kervidy-Naizin watershed. Therefore, stream DOC patterns seem to be controlled by DOC source characteristics (i.e., limited or not) connected to the stream by groundwater dynamics.

In addition to studies that demonstrate the tight link between changes in water flow paths and change in stream DOM features, several studies highlight impacts of climate factors on variations in stream DOC concentrations. Therefore, the role of temperature has been emphasized to explain seasonal stream DOC variability [e.g., *Dawson et al.*, 2011, 2008; *Winterdahl et al.*, 2011], and antecedent soil moisture conditions have been emphasized to explain stream DOC concentrations after hydrological events [e.g., *Inamdar et al.*, 2008; *Turgeon and Courchesne*, 2008]. Commonly suggested mechanisms that increase DOC concentrations after rewetting involve the mobilization of (i) microbial biomass that died through drying [*Christ and David*, 1996], (ii) products of soil organic matter (SOM) decomposition-mineralization that occur during wet-dry cycles [*Chow et al.*, 2006], and (iii) previously sequestered carbon made available by soil structure disruption that cause wet-dry cycles [*Lundquist et al.*, 1999]. Furthermore, biological and physicochemical processes that occur under reducing conditions can also increase DOC concentrations in saturated soils [e.g., *Grybos et al.*, 2009].

Groundwater level variations resulting from climate conditions and hydrological control can regulate both DOC accumulation in soils and DOC transfer to streams, two antagonistic processes that are involved in flushing solutes [*Burns*, 2005]. *Mehring et al.* [2013] demonstrated that a longer period of low discharge (i.e., the dry season in temperate watersheds) reduced DOC export downstream and increased DOC concentrations in the subsequent hydroperiod in the Suwannee River basin, U.S. However, the effects of groundwater dynamics on stream DOM features are usually considered at the event scale [e.g., *Inamdar et al.*, 2008; *McGlynn and McDonnell*, 2003; *Morel et al.*, 2009; *Turgeon and Courchesne*, 2008] and the seasonal scale [e.g., *Lambert et al.*, 2013, 2014; *Laudon et al.*, 2011; *Sanderman et al.*, 2009] but rarely at the annual scale.

This study aims to assess how intra-annual variations in hydroclimatic factors impact the annual variability of stream DOC concentrations and fluxes from 13 years of monitoring in the research watershed of Kervidy-Naizin. No significant year-to-year change in land use or practices are expected to have occurred during the study period since cropping systems are relatively stable in this agricultural area [*Salmon-Monviola et al.*, 2013]. Consequently, we assume that the hydroclimate controls the interannual variations. Specific objectives are (i) to study the hydrochemistry response of the watershed to a wide range of climate conditions, (ii) to relate 13 years of intra-annual stream DOC dynamics to the conceptual model that links DOC sources and DOC transfer suggested by 1 year studies, and (iii) to identify the seasonal controls of interannual variability in stream DOC concentrations and fluxes.

2. Materials and Methods

2.1. Study Watershed

The 5 km^2 Kervidy-Naizin headwater watershed is located in Brittany (western France; Figure 1a) and is drained by an intermittent stream of 2nd Strahler order. Since 2002, it has belonged to the AgrHyS environmental research observatory (http://www6.inra.fr/ore_agrhys_eng) and is part of the French RBV Catchment Network (http://rnbv.ipgp.fr/?page_id=1122). The research conducted in this area focuses on the response times of water quality to intensive agriculture and climate forcing.

Elevation ranges from 93 to 135 m above sea level, with gentle slopes <5%. The watershed lies on impervious bedrock of Brioverian schists that are locally fractured. The groundwater is shallow in a 1–30 m thick layer of impaired schists material, with level variations of 7 m in upland domains to less than 1 m in bottomland domains. Upland areas consist of well-drained soils (Haplic Luvisols), while bottomland areas consist of hydromorphic soils (Epistagnic Haplic Luvisols and Epistagnic Haplic Albeluvisols) [*Curmi et al.*, 1998; *FAO*, 2006]. The organomineral layers are 30–40 cm deep in the cultivated hillslopes and decrease to about 20 cm deep in bottomland areas. Soil carbon contents (C_{org}) and DOC concentrations in soil solution samples show a tenfold vertical decrease from organomineral soil horizons (4.4% and 10.9 mg C L^{-1} for C_{org} and DOC, respectively) to underlying mineral soil horizons (0.4% and 1.5 mg C L^{-1}, respectively) [*Lambert*

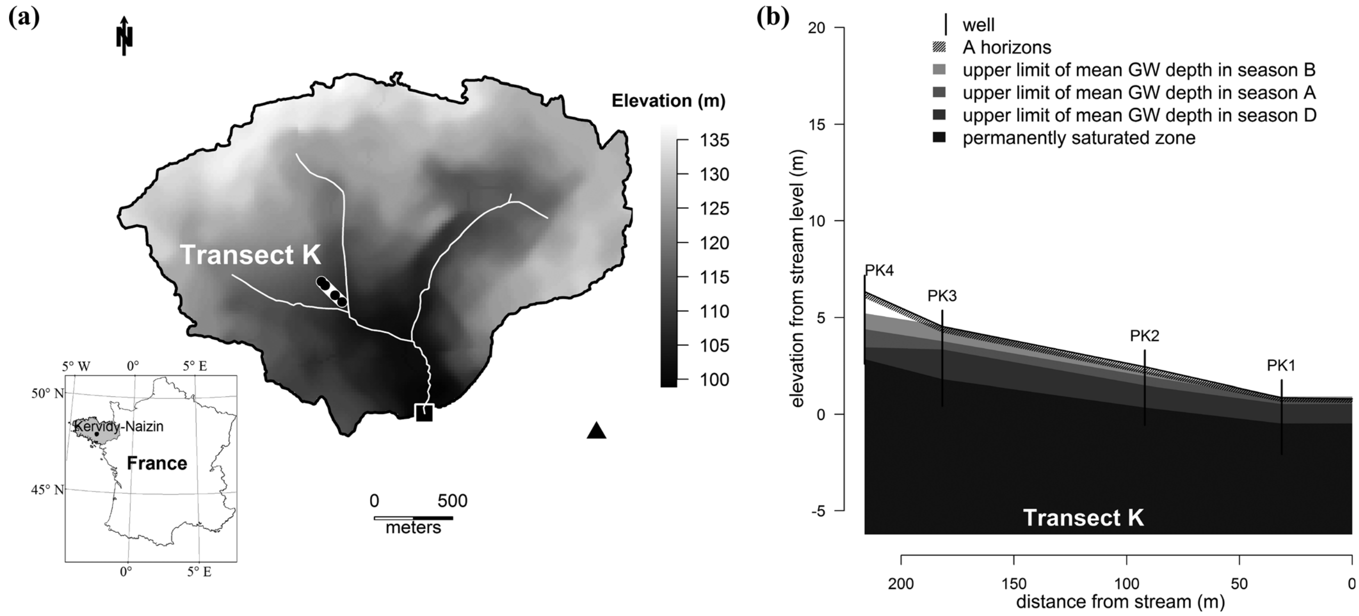

Figure 1. (a) Location in France and in Brittany (gray area in inset map) and topographic map of the Kervidy-Naizin watershed. Black dots show locations of wells on one transect (thick white line). The gauging station at the outlet of the watershed and the weather station are shown as a square and a triangle, respectively. (b) Simplified representation of interannual variations in groundwater (GW) level averaged by season along the well transect K.

et al., 2011; *Morel et al.*, 2009]. Further, a lateral increase in topsoil C_{org} is observed, from 1.1% on hillslopes to 4.4% in wetland domains.

The hydrology is controlled by groundwater fluctuations along the hillslopes at seasonal and event scales. A succession of three hydrological seasons for this watershed has been identified in streamflow chemistry studies [*Aubert et al.*, 2013; *Lambert et al.*, 2013; *Molenat et al.*, 2008]. Season A: rewetting of riparian wetland soils after the dry summer season; season B: rise of groundwater in the upland domain that leads to prolonged waterlogging of wetland soils and establishes a marked hydraulic gradient in groundwater between upland and wetland domains; and season C: drawdown of groundwater leading to drying of the stream (Figure 1b).

The climate is temperate oceanic, with annual rainfall and annual specific discharge averaging 830 and 320 mm yr^{-1}, respectively, from 2000 to 2013. The daily temperature averaged 11°C over the period 2000–2013.

Land use is mostly agricultural and is subdivided into cereal crops (20%), maize (30%), and grassland (20%), with 30% other land uses, such as woods, buildings, gardens, and roads. The wetland domains are buffer strips of grassland and trees, while hillslope domains are arable crops and pastures. The stream draining this landscape is neutral, with a mean pH of 7 and a mean electrical conductivity of 267.4 μS cm^{-1}, due mainly to high N-NO_3^- concentrations (16.5 $\pm$ 2.8 mg N-NO_3^- L^{-1}over the period 2000–2013).

2.2. Data Acquisition

Hourly rainfall data, hourly air temperature data, daily extreme soil temperatures 10 cm belowground, and parameters used to compute daily potential evapotranspiration from the Penman formula [*Penman*, 1948] were recorded at the weather station, approximately 1 km east of the watershed outlet. From 2001, groundwater depth was recorded at 15 min intervals using pressure sensors (Orpheus Mini OTT, accuracy of $\pm$2 mm) along a transect of 2–10 m deep piezometers (transect K; Figure 1). Groundwater variations recorded at piezometers PK1, PK2, and PK4 along transect K (Figure 1b) were assumed to represent those in the wetland, middle-slope, and upland domains of the watershed, respectively. Stream discharge was gauged from stream levels recorded every minute using a float-operator sensor (Thalimèdes OTT, accuracy of $\pm$2 mm).

Stream water composition (DOC, NO_3^-) was determined from daily samples collected in the afternoon (2–9 p.m.), except in 2002–2003, when the sampling frequency was reduced to once every 2–4 days. Water samples were filtered immediately at 0.2 μm and stored in the dark at 4°C in propylene bottles until analysis

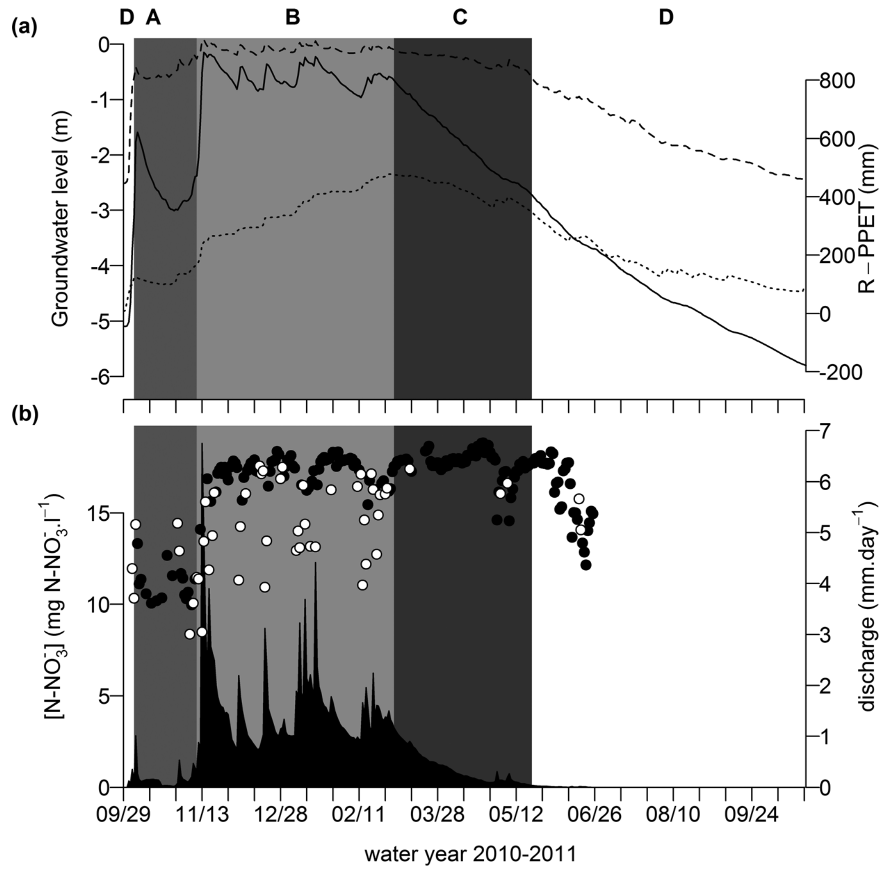

Figure 2. (a) Groundwater level in the upland domain (piezometer PK4; solid line) identifies the transition between seasons A (medium gray area) and B (light gray area). The maximum difference between cumulative rainfall (R) and cumulative Penman potential evapotranspiration (PPET; dotted line) identifies the transition between seasons B and C (dark gray area). Season D (dry season; white area) is identified from groundwater level in the wetland domain (PK1; dashed line). D extends from the first decrease of groundwater below −30 cm to its first increase above this depth. (b) Discharge (black area) and [N-NO_3^-] of base flow (black circles) and stormflow (white circles).

(within 2 weeks). Major anion concentrations were measured by ionic chromatography (DIONEX DX 120). DOC concentrations were determined from the difference between total dissolved carbon and dissolved inorganic carbon, both measured with a total organic carbon analyzer (Shimadzu TOC-5050A and Shimadzu TOC-V_{CSH} for 2009, accuracy of 5%).

2.3. Definition and Calculation of Hydrological Periods

The data set used for this study includes 13 water years from October 2000 to September 2013. Within each year, seasons were defined from fluctuations in groundwater level. The dry season (D) was defined as the time period when groundwater remained below a depth of 30 cm at the lowest piezometer (PK1). This depth approximates the maximum thickness of the organomineral horizon at this location, and D was therefore assumed to represent the period when all organomineral horizons of the watershed remain unsaturated. Two other transition indices were defined to divide the wet period into the three hydrological seasons defined above. The transition between season A and B was identified as the rapid increase (generally occurring within few days) to a high groundwater level in the upland domain (PK4) (Figure 2a). A marked increase in stream NO_3^- concentrations between A and B is well known for this watershed and hence can assist in the determination (Figure 2b) [*Molenat et al.*, 2008]. The transition between seasons B and C was identified as the maximum difference between cumulative rainfall and cumulative Penman potential evapotranspiration (Figure 2a). Twelve successive sequences of dry seasons (D) followed by wet seasons (A, B, and C) of various lengths were obtained from the current data set.

Within each hydrological season, stormflow was separated from base flow based on a change in water level recorded at the outlet. Based on a 3 h difference in mean hourly water level, a storm event started when

Table 1. Variables Run in Partial Least Squares Regressions (PLSR)[a]

Variables	Unit	DOC[b]	[DOC][b]
DOC variables			
DOC flux	kg DOC ha^{-1} yr^{-1}	Y	
Stormflow DOC flux	kg DOC ha^{-1} yr^{-1}	Y	
Base flow DOC flux	kg DOC ha^{-1} yr^{-1}	Y	
Mean [DOC]	mg C L^{-1}	X	Y
Stormflow mean [DOC]	mg C L^{-1}	X	Y
Base flow mean [DOC]	mg C L^{-1}	X	Y
Mean seasonal [DOC][c]	mg C L^{-1}	X	
Base flow mean seasonal [DOC][c]	mg C L^{-1}	X	
Stormflow mean seasonal [DOC][c]	mg C L^{-1}	X	
Annual and seasonal variables			
Duration	day	X	X
Mean temperature	°C	X	X
Cumulative soil temperatures (−0.1 m)	°C d	X	X
Cumulative rainfall	mm	X	X
Wetland groundwater (GW) depth	m	X	X
Middle-slope GW depth	m	X	X
Upland GW depth	m	X	X
Mean discharge[c]	L s^{-1}	X	X
Base flow mean discharge[c]	L s^{-1}	X	X
Stormflow mean discharge[c]	L s^{-1}	X	X
Runoff[c]	mm	X	X
Base flow runoff[c]	mm	X	X
Storm runoff[c]	mm	X	X
Number of events[c]	day	X	X
Number of base flow days	day	X	X
Storm frequency[c]	d d^{-1}	X	X
Ratio of storm runoff to runoff[c]	mm mm^{-1}	X	X

[a]X, explanatory variable used in PLSR; Y, variable explained in PLSR.
[b]Variables to explain in PLSR; DOC, DOC flux; [DOC], DOC concentration.
[c]Not calculated in season D.

the difference first exceeded 4 mm and ended when it first decreased below 2 mm. Consequently, daily concentration from grab sampling (2–9 p.m.) during a storm event was classified as stormflow.

2.4. Variables and Statistical Analyses

DOC flux and mean DOC concentrations were calculated for each water year, each season, and each flow-type considered within a year or within a season (base flow, stormflow, base flow + stormflow; Table 1). All mean DOC concentrations were discharge-weighted. To assess DOC fluxes, a missing value was approximated using the mean concentration calculated under hydrological conditions similar to those of the day when the missing value occurred. For instance, missing values for DOC concentration of base flow in season A in water year 2002–2003 were approximated by the mean DOC concentration for base flow of that same season. Within each water year, <25% of the days had missing concentrations.

Normalized runoff was calculated as *x* axis to present the seasonal and annual dynamics of daily DOC concentrations. Normalized annual runoff was calculated by dividing cumulative runoff on a given day by cumulative runoff in the day's water year. Similarly, seasonal normalized runoff was calculated by dividing cumulative runoff on a given day by cumulative runoff in the day's hydrological season considered.

Duration, climate, and hydrological indices were calculated for each season and for each flow-type considered as potential explanatory variables of interannual variability in fluxes and concentrations (Table 1). Climate indices included cumulative rainfall and mean and cumulative soil temperatures. Hydrological indices included mean discharge, runoff, number of events, storm frequency, and ratio of storm runoff to runoff in the period considered. Mean groundwater depths in the wetland domain (PK1), middle-slope domain (PK2), and upland domain (PK4) were also calculated within periods. Hereafter, when concentration and flux data do not refer to any specific flow-type, they were calculated by considering both stormflow and base flow days combined.

Normality and homoscedasticity tests were performed first (tests of Shapiro-Wilk and Bartlett, respectively) to compare seasonal variations in mean DOC concentrations calculated for each flow-type. Bilateral and unilateral Student's *t* tests were then performed to compare means calculated on a seasonal and flow-type basis, respectively. Time series for DOC concentrations and hydroclimatic variables were estimated with a linear regression trend line (±95% confidence intervals) to assess potential changes over the time period under investigation [*Dawson et al*., 2008; *Monteith et al*., 2001]. In addition, the temporal autocorrelation was assessed for annual mean DOC concentrations with lag ranging from 1 to 11 year.

The influence of seasons on interannual variability in annual DOC fluxes and mean annual DOC concentrations over 12 years was investigated by combining partial least squares regressions (PLSRs) and both simple and multiple linear regressions (SLR and MLR, respectively; supporting information Figure S1). Since 12 observations were used in PLSRs and linear regressions, we assumed that linear models were reliable enough. PLSRs were run to select the most relevant explanatory variables, which were often cross-correlated and much more numerous than the number of observations [*Mehmood et al*., 2012; *Tenenhaus*, 1998]. A forward stepwise regression (FSR) [*Morel et al*., 2009] was then run with the most important variables selected in PLSRs to facilitate interpretation of results. FSR aimed to optimize the adjusted R^2 (hereafter R^2) by using independent variables. Relationships between variables included in the regressions were explored using the Pearson correlation coefficient r.

Each explained variable was analyzed individually in the PLSRs. Temporal and hydroclimatic variables calculated for antecedent dry seasons (D) and hydrological seasons were taken separately (A, B, or C) or together (ABC) and were included as explanatory variables. Since mean seasonal or annual concentrations could control annual fluxes, they were included as predictors in PLSRs run for annual fluxes. Explanatory variables were normalized (i.e., by subtracting the mean and dividing by the standard deviation) prior to each analysis. The most relevant variables out of 87 and 75 for PLSR for fluxes and concentrations, respectively, were selected by backward variable selection (BVSPLS) [*Pierna et al*., 2009]. From an initial model that included all predictors, refined models were generated stepwise by removing the least significant variable, identified with a leave-one-variable-out validation method (i.e., deleting one variable at a time). The best model was finally identified using the root-mean-square error of prediction (RMSEP) as a selection criterion [*Pierna et al*., 2009]. The regressions performed then focused on the predictors of the best PLSRs with variable importance in projection (VIP) > 1 [*Mehmood et al*., 2012]. Altogether, six BVSPLS-FSRs were performed to explain annual DOC fluxes and mean annual DOC concentrations calculated for each flow-type (stormflow, base flow, stormflow + base flow).

Statistical analyses were performed with the R open-source software [*R Core Team*, 2014], and PLSRs were performed with the *pls* package [*Mevik and Wehrens*, 2007] according to the classic orthogonal scores algorithm.

3. Results

3.1. Temperature, Runoff, and Groundwater Variations

Temperature and rainfall dynamics recorded between October 2000 and September 2013 exhibited patterns typical of temperate regions under oceanic influence, with some extreme events (Figure 3a and Table 2). Daily air temperature averaged 11.2 ± 5.2°C (mean ± standard deviation (SD)), with a moderate range of variations between winter (5.8 ± 3.7°C) and summer (16.7 ± 2.6°C). This did not preclude the existence of strong fluctuations in the short term: a fairly cold winter and fairly hot summer with minimum and maximum daily mean air temperatures <-4 and >29°C, respectively, occurred during the study period (water year 2002–2003). Similarly, rainfall amounts averaged 829.6 ± 193.7 mm yr^{-1}, with very wet (1327 mm yr^{-1}; water year 2000–2001) and very dry (488 mm yr^{-1}; water year 2004–2005) years observed during the 13 years of monitoring.

Maximum stream discharge and annual runoff varied strongly within standard seasonal patterns (Figure 3b and Table 2). Maximum daily discharge reached 10 mm d^{-1} in water years 2006–2007 and 2009–2010 and even 18 mm d^{-1} in 2000–2001, but did not exceed 2 mm d^{-1} in 2004–2005. Annual runoff varied by a factor >6, ranging from 111 to 741 mm in 2004–2005 and 2000–2001, respectively.

Groundwater level and duration of soil water saturation also experienced strong interannual variations over the study period (Figure 3c and Table 2). The length of the dry season D ranged from about 1 month (2000–2001, 2003–2004, and 2007–2008) to more than 5 months (2002–2003, 2004–2005, and 2010–2011).

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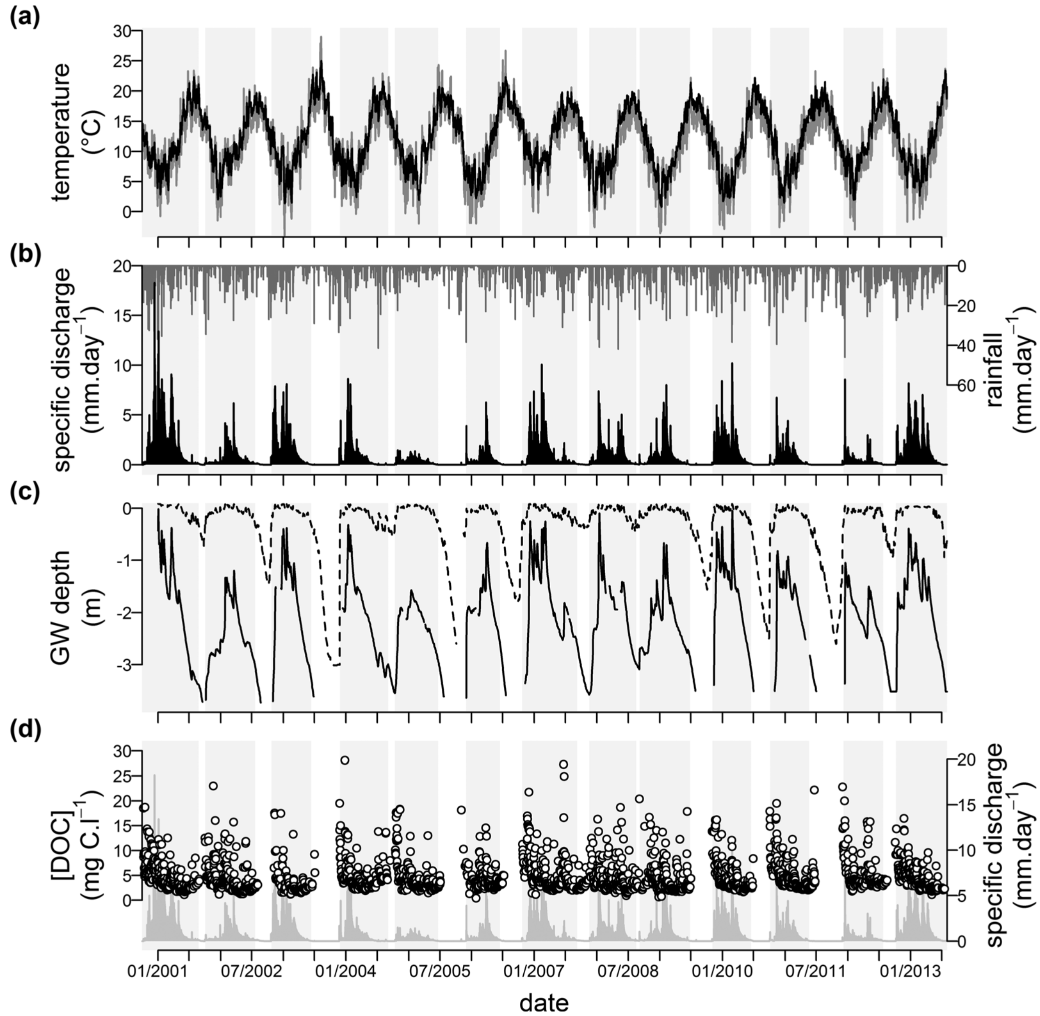

Figure 3. Variations in seasons, temperature, rainfall, discharge, groundwater table (GW) depth, and dissolved organic carbon (DOC) concentrations over the study period. Wet and dry seasons are superimposed onto each plot in gray and white, respectively. Due to an absence of GW measurements, no dry season is identified before 1 January 2001. (a) Air and soil (−0.1 m) temperatures (gray and black lines, respectively). (b) Daily rainfall (gray lines) and daily discharge (black line). (c) Groundwater dynamics in wetland (dashed line) and upland soils (solid line). (d) Daily DOC concentrations (unfilled black circles) and daily discharge (gray line).

As a result, the maximum depth to the water table in wetland domains during season D was also extremely variable, ranging from 0.385 m in 2006–2007 to 3.014 m in 2002–2003. In season B, although groundwater continuously waterlogged the wetland domain regardless of year (0 ± 0.027 m), its level in the upland domain fluctuated strongly, reaching the topsoil (>-0.1 m) in some years (2000–2001, 2007–2008, and 2009–2010) and remaining below 1 m deep in other years (2001–2002, 2004–2005, and 2011–2012).

Small but significant ($p < 0.05$) trends of increasing daily soil temperatures and decreasing discharge and groundwater levels in wetland and middle-slope domains were observed over the study period. No significant trend was observed for other climatic variables (i.e., daily air temperature or rainfall).

3.2. DOC Fluxes and Annual Means of DOC Concentrations

Annual DOC fluxes at the outlet of the Kervidy-Naizin watershed ranged from 5.4 to 39.5 kg of DOC ha^{-1} yr^{-1} and were controlled by water fluxes (Figure 4a). Within water years, most DOC fluxes were exported in the periods of high discharge, i.e., in season B ($84 \pm 9\%$) and during storm events ($61 \pm 9\%$) regardless of their relative durations.

In marked contrast with this strong interannual variability in DOC fluxes, mean annual concentrations were relatively stable (Figure 4b and Table 2). Mean annual DOC concentrations ranged from 4.9 to 7.5 mg C L^{-1}

Table 2. Seasonal and Interannual Variability in Climatic and Hydrologic Variables and Dissolved Organic Carbon (DOC) Concentrations[a]

	Season	00-01	01-02	02-03	03-04	04-05	05-06	06-07	07-08	08-09	09-10	10-11	11-12	12-13	Mean	SD
								Soil Temperature (°C)								
Mean	A	12.1	8.8	12.3	7.2	12.5	NA	12.1	5.7	13.0	10.4	12.2	9.3	15.0	10.9	2.7
Mean	B	8.3	8.7	7.3	6.5	7.7	5.8	8.4	9.4	6.0	6.0	6.1	8.4	7.7	7.4	1.2
Mean	C	17.0	13.8	11.9	15.2	11.7	13.1	15.1	17.9	12.6	12.9	11.9	16.9	14.0	14.2	2.1
Mean	ABC	12.1	10.8	9.5	11.9	9.7	8.5	12.6	11.1	9.9	8.3	9.1	11.1	9.8	10.3	1.4
Mean	D	16.1	16.1	16.8	15.7	15.7	17.9	12.0	17.1	16.5	17.8	15.9	17.6	n.a.	16.3	1.6
								Rainfall (mm)								
Sum	D	74	203	311	57	262	260	38	48	227	236	363	151	n.a.	186	110
								Water Runoff (mm)								
Sum	A	3.6	35.1	4.3	14.8	3.5	0.0	1.7	15.6	10.1	0.4	5.9	0.2	7.5	7.9	9.7
Sum	B	683.7	111.9	358.0	178.7	77.5	108.4	307.0	256.6	216.2	372.3	179.6	116.4	426.5	261.0	169.7
Sum	C	53.8	72.5	57.8	49.6	29.9	55.2	133.5	32.5	48.1	35.2	29.5	18.4	45.0	50.8	28.8
Sum	ABC	741.1	219.4	420.0	243.1	111.0	163.6	442.2	304.7	274.4	407.9	215.0	134.9	479.0	319.7	174.9
								Mean Discharge ($l.s^{-1}$)								
Mean	A	10.2	17.6	27.0	30.0	14.3	n.a.	3.6	18.8	9.9	4.2	9.6	2.6	53.0	16.7	14.4
Mean	B	208.5	109.4	165.1	123.6	34.3	50.0	158.3	96.4	98.1	142.7	90.1	43.1	133.6	111.8	51.1
Mean	C	21.1	34.5	33.1	16.4	15.4	42.3	41.4	24.9	24.6	27.7	21.2	14.3	31.1	26.8	9.3
Mean	ABC	119.7	42.9	103.1	49.1	25.0	47.1	78.4	63.5	52.9	102.8	53.7	33.3	99.0	67.0	30.4
								Duration (day)								
Sum	D	38	96	168	39	163	129	71	20	130	112	200	76	n.a.	104	57
								Wetland Groundwater Depth (m below surface)								
Mean	A	n.a.	0.085	0.176	0.109	0.136	n.a.	0.247	0.099	0.123	0.216	0.332	0.241	0.104	0.170	−0.079
Mean	B	n.a.	−0.039	−0.024	−0.006	−0.035	0.039	−0.028	−0.018	−0.008	0.003	0.001	0.049	−0.012	−0.007	−0.027
Mean	C	0.152	0.078	0.112	0.193	0.048	0.099	0.129	0.222	0.091	0.140	0.115	0.061	0.097	0.118	−0.050
Mean	D	0.524	0.846	1.945	0.444	1.147	1.186	0.344	0.340	0.866	1.501	1.378	0.640	n.a.	0.930	−0.510
								Upland Groundwater Depth (m below surface)								
Mean	A	n.a.	2.799	3.731	1.940	3.266	n.a.	3.266	2.787	2.729	3.731	3.308	3.731	2.968	3.114	−0.546
Mean	B	n.a.	1.620	1.367	1.224	1.901	1.767	1.118	1.483	1.707	1.221	1.415	1.901	1.356	1.507	−0.269
Mean	C	2.729	2.420	2.358	2.467	2.383	1.896	2.062	2.370	2.377	2.348	2.054	2.195	2.308	2.305	−0.212
Mean	D	3.525	3.370	3.442	3.300	3.258	3.086	3.182	3.034	3.179	3.282	3.185	3.240	n.a.	3.257	−0.141
								Mean DOC Concentration ($mg\ C.l^{-1}$)								
Mean	A	9.0	4.9	9.2	8.7	13.1	n.a.	8.7	5.2	11.9	9.4	11.0	9.4	10.3	9.2	2.4
Mean	B	5.5	6.5	6.1	6.3	5.2	6.1	6.4	5.4	5.4	5.8	6.5	8.1	5.4	6.1	0.8
Mean	C	2.4	2.7	2.2	3.5	3.2	3.5	4.5	3.1	2.9	2.4	2.7	3.8	2.5	3.0	0.7
Mean	ABC	5.4	4.9	5.5	5.9	4.9	5.2	5.9	5.2	5.0	5.6	6.1	7.5	5.1	5.5	0.7

[a]D: drought; A: rewetting; B: high flow; C: recession; and SD: standard deviation.

and were poorly correlated with annual water runoff ($r = -0.17$, $p = 0.59$) or mean discharge ($r = -0.12$, $p = 0.70$). Noticeably, the highest mean concentrations (>5.6 mg C L^{-1}) occurred in water years that followed warm summers with deep drawdown of groundwater in the wetland domain (2003–2004, 2006–2007, 2010–2011, and 2011–2012). However, this impact of summer drought on mean annual concentration, if any, did not affect any other water year but the one next its occurrence, as shown by low mean annual DOC concentration recorded in 2004–2005 (4.9 mg C L^{-1}). Furthermore, no trend of daily DOC concentration (Figure 4b; $r^2 < 0.001$, $p = 0.3$) and no significant periodicity in mean annual DOC concentrations were found. The temporal autocorrelation coefficients ranged from −0.21 to 0.15 (0.1 ± 0.07 in absolute values).

3.3. Intra-annual and Interannual Variability of DOC Concentrations

Intra-annual dynamics of DOC concentrations displayed comparable patterns, with a marked decrease in daily DOC in season A, followed by an even greater decrease during seasons B–C (Figures 3d and 5a). Thus, mean seasonal DOC concentrations significantly ($p < 0.001$) decreased from 9.2 ± 3.0 mg C L^{-1} in A to 6.1 ± 0.8 mg C L^{-1} in B and down to 3.0 ± 0.7 mg C L^{-1} in C (Table 2). Four typical features describe intra-annual DOC dynamics: (i) slopes of regressions between concentrations and normalized runoff decreased from seasons A to B; (ii) within each season, stormflow concentrations decreased quicker than base flow concentrations (Figures 5a and 5b); (iii) between the end of A and beginning of B, concentrations of both flow-types increased from ca. 1–3 to 5–9 mg C L^{-1} (Figure 5a); and (iv) base flow concentrations neared a constant value of ca. 2–3 mg C L^{-1} at the end of B, regardless of the water year considered.

Regressions between daily DOC concentrations and daily normalized runoff indicate that the interannual variation in concentrations was weaker at the end than at the beginning of the season (Figure 5b).

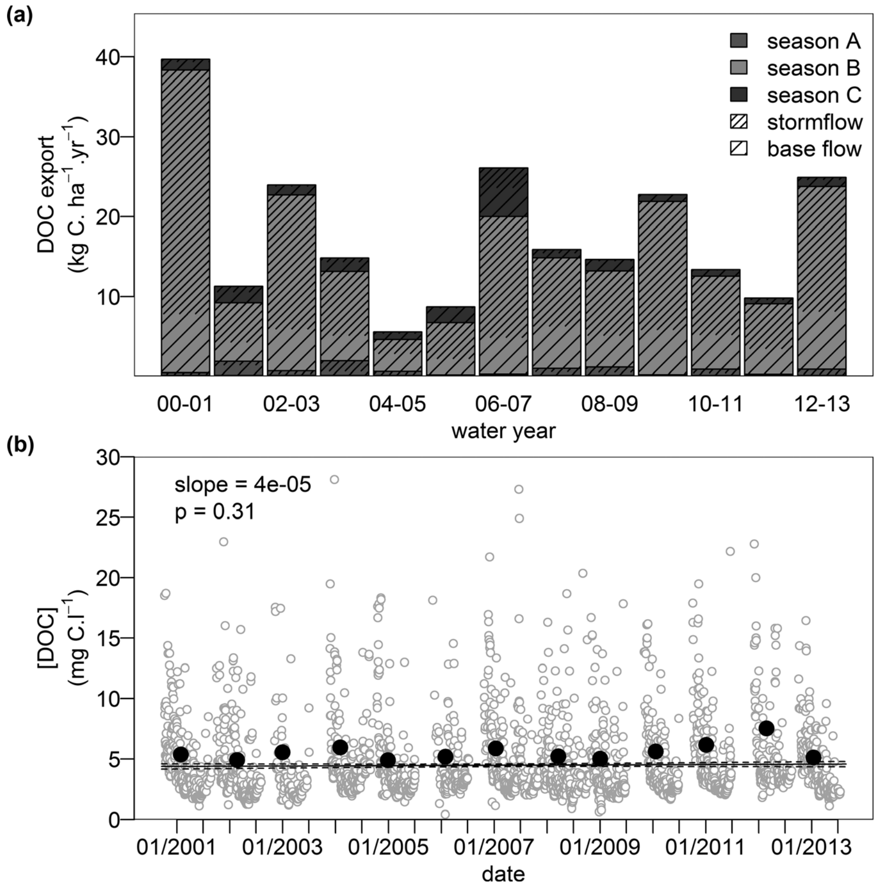

Figure 4. (a) Interannual variability of dissolved organic carbon (DOC) fluxes. Season A: rewetting, season B: high flow, and season C: recession. (b) Interannual variability of discharge-weighted mean of annual DOC concentrations (black circles). No trend of daily DOC concentrations (unfilled gray circles) is found by linear regression and its 95% confidence interval (solid and dashed lines, respectively).

Figure 5c and Table 2 show interannual differences of DOC dynamics from relationships between daily concentrations and daily water runoff without normalization. Higher DOC concentrations occurred in season B of the dry year (2011–2012; 8.1 mg C L^{-1}) than in the wet year (2012–2013; 5.4 mg C L^{-1}) (Figure 5c and Table 2), which indicates that water flux can affect concentrations at the end of the season.

Within each period stream DOC concentrations were higher in stormflow than in base flow, and their seasonal dynamics differed by flow-type (Figure 5).

3.4. PLSR Model Results

Figures 6 and supporting information Figure S2 show the weight of the most important predictors selected through the BVSPLS procedure (i.e., VIP > 1) that explains mean DOC concentrations and DOC fluxes. They indicate the strength of the correlation of predictors with the PLS responses and thus with the variable to explain.

The factors selected by PLSR confirmed that runoff was the main factor controlling interannual variations in DOC fluxes regardless of the flow-type considered (supporting information Figure S2). The variables linked to the wetness of wet seasons and especially to the wetness of B seasons (runoff, mean discharge, occurrence, and frequency of storm events) were all highly correlated with each other and positively correlated with annual DOC flux. For SLRs, annual runoff explained more than 90% of variations in annual DOC fluxes and base flow DOC fluxes, and annual runoff in storm events explained 95% of variations in stormflow DOC fluxes (supporting information Figure S3).

However, the PLSRs run to explain interannual variations in mean annual DOC concentrations selected additional controlling factors (Figure 6). The PLSRs sufficiently predicted the mean annual concentration calculated for the entire water year (stormflow + base flow; $Q^2Y = 0.66$; Figure 6a). Duration and intensity of seasons D and wetness of seasons A and B were the main controlling factors selected by this PLSR (VIP > 1). Duration and intensity

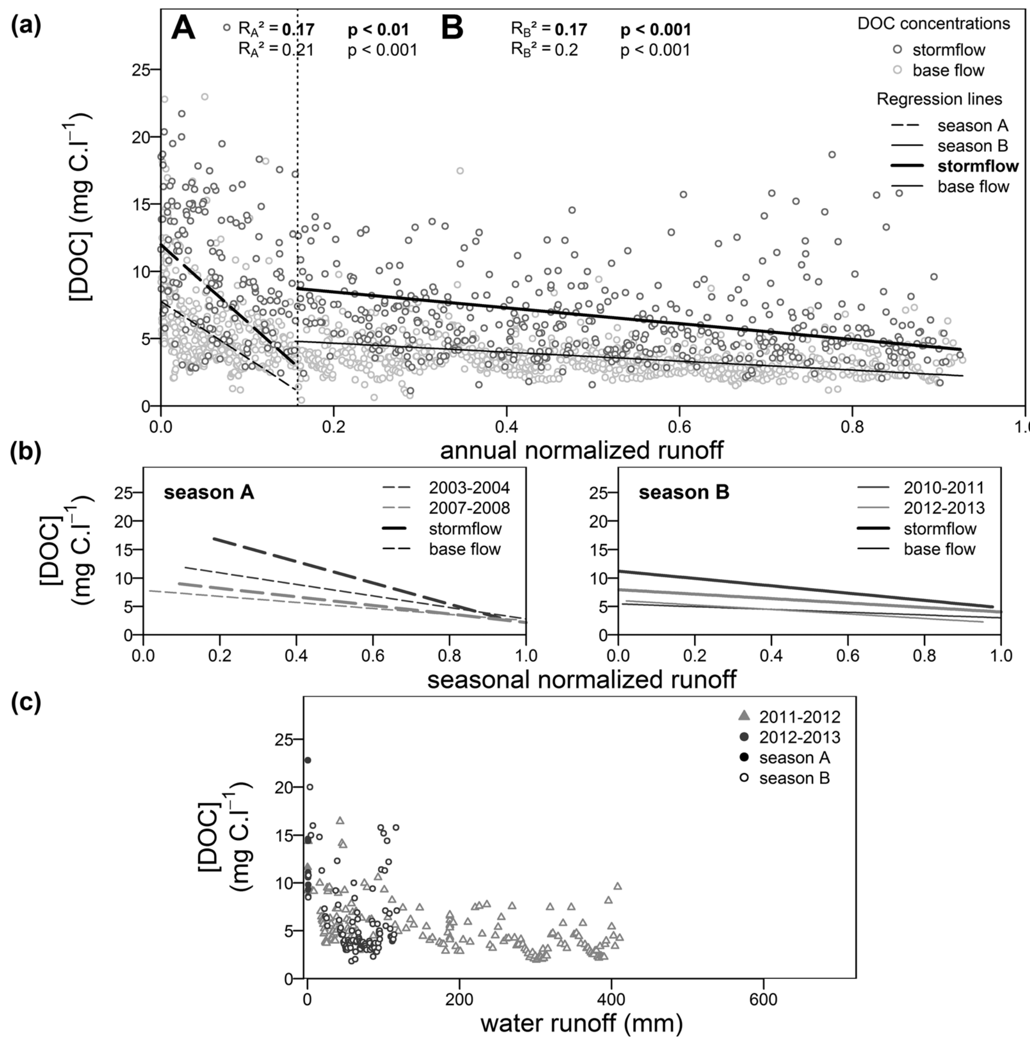

Figure 5. (a) Evolution of daily dissolved organic carbon (DOC) concentrations as a function of annual normalized runoff, which equals cumulative runoff at the time that DOC concentration is measured divided by annual water runoff. The vertical line marks the maximum normalized runoff of transition between seasons A and B. (b) Examples of stream DOC dynamics recorded for stormflow and base flow for contrasting years during seasons A and B (left and right, respectively). The *x* axis is cumulative seasonal runoff at time that DOC concentration is measured divided by the seasonal runoff. (c) Daily DOC concentrations in 2011–2012 and in 2012–2013 in water runoff in seasons A and B of these water years.

of seasons D were expressed by five highly correlated variables ($|r| > 0.72$, $p < 0.01$) that all positively controlled the mean annual concentration. Three out of the five variables were linked to the length of season D (i.e., cumulative soil temperatures, cumulative rainfall and duration), while the two others were linked to the drawdown of groundwater in season D (mean groundwater depths in middle-slope and wetland domains). The length of the season D was positively correlated with the drawdown of the water table within this season ($r = 0.83$, $p < 0.001$). The positive relationship between the mean groundwater depth expressed in meter below surface and annual mean DOC concentration (Figure 6a) was consistent with an increase in concentrations due to seasonal drought. Therefore, both rainfall and number of events in season A lowered the mean concentration while the mean groundwater depth increased it, which was consistent with a general negative impact of wetness on mean annual DOC concentrations in season A. The mean groundwater depth in the wetland domain in season B, though barely variable from year-to-year (SD = 0.027 m), increased the mean annual DOC concentrations.

The PLSRs sufficiently predicted interannual variations in stormflow mean DOC concentrations ($Q^2Y = 0.48$; Figure 6b). The wetness in seasons A, B, or ABC together expressed by variables such as storm frequency, runoff, or mean discharge lowered stormflow mean annual DOC concentrations. The selected variables related to wet conditions in season A were highly correlated with each other ($|r| > 0.76$, $p < 0.01$) but did not correlate much with other indices of wetness conditions ($|r|$ ranging from 0.14 to 0.66). Among the variables linked to

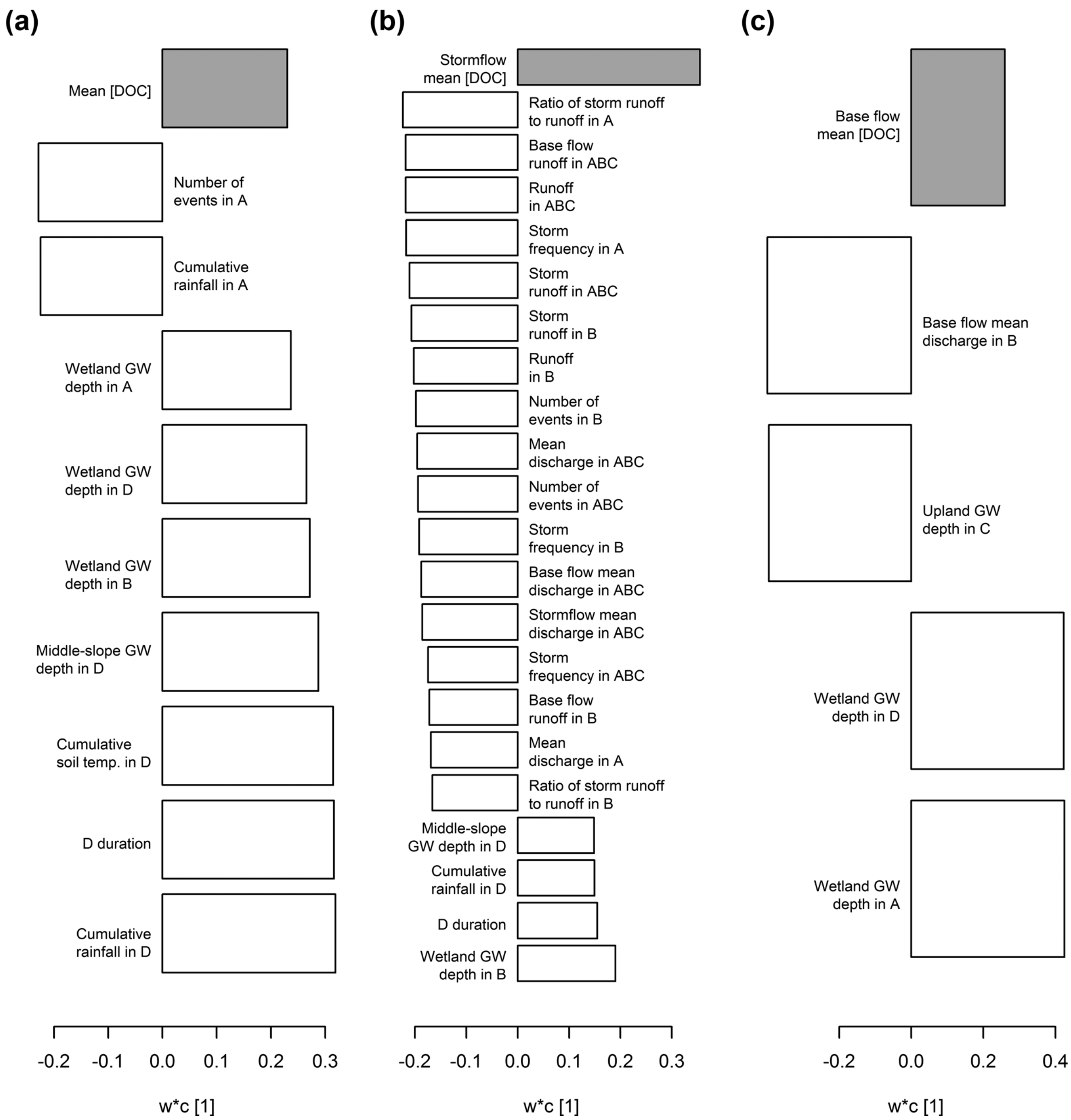

Figure 6. PLS weight plot for the most important variables (variable importance in projection > 1) selected through backward variable selection in partial least squares regression for two-component models that explain (a) mean annual DOC concentration: $R^2Y = 0.90$, $Q^2Y = 0.66$, 9 of 23 variables remained important; (b) stormflow mean annual DOC concentration: $R^2Y = 0.87$, $Q^2Y = 0.48$, 21 of 37 variables remained important; (c) base flow mean annual DOC concentration: $R^2Y = 0.93$, $Q^2Y = 0.80$, 4 of 7 variables remained important. Variables to explain and explanatory variables are showed with gray bars and white bars, respectively. D: drought; A: rewetting; B: high flow; C: recession; DOC: dissolved organic carbon; GW: groundwater table.

season B or to the entire wet season (i.e., ABC), wetland groundwater depth in B was the only one that was not correlated with the others ($|r| < 0.49$). The length and intensity of the season D expressed as D duration and middle-slope groundwater depth in D, respectively, positively influenced stormflow mean DOC concentration.

The PLSRs sufficiently predicted interannual variations in base flow mean DOC concentrations ($Q^2Y = 0.80$; Figure 6c). Among the variables selected, drawdown of groundwater in the wetland domain during seasons D and A increased mean concentration, while base flow mean discharge in season B lowered it. Surprisingly, mean groundwater depth in the upland domain in season C is negatively correlated with mean groundwater depth in the wetland domain in season A ($r = -0.86$, $p < 0.001$) and negatively affected base flow mean annual DOC concentration.

From the factors indicated by each PLSR, FSRs were performed to model variations in mean annual DOC concentration for each flow-type (stormflow + base flow, stormflow, base flow; Figures 7 and supporting

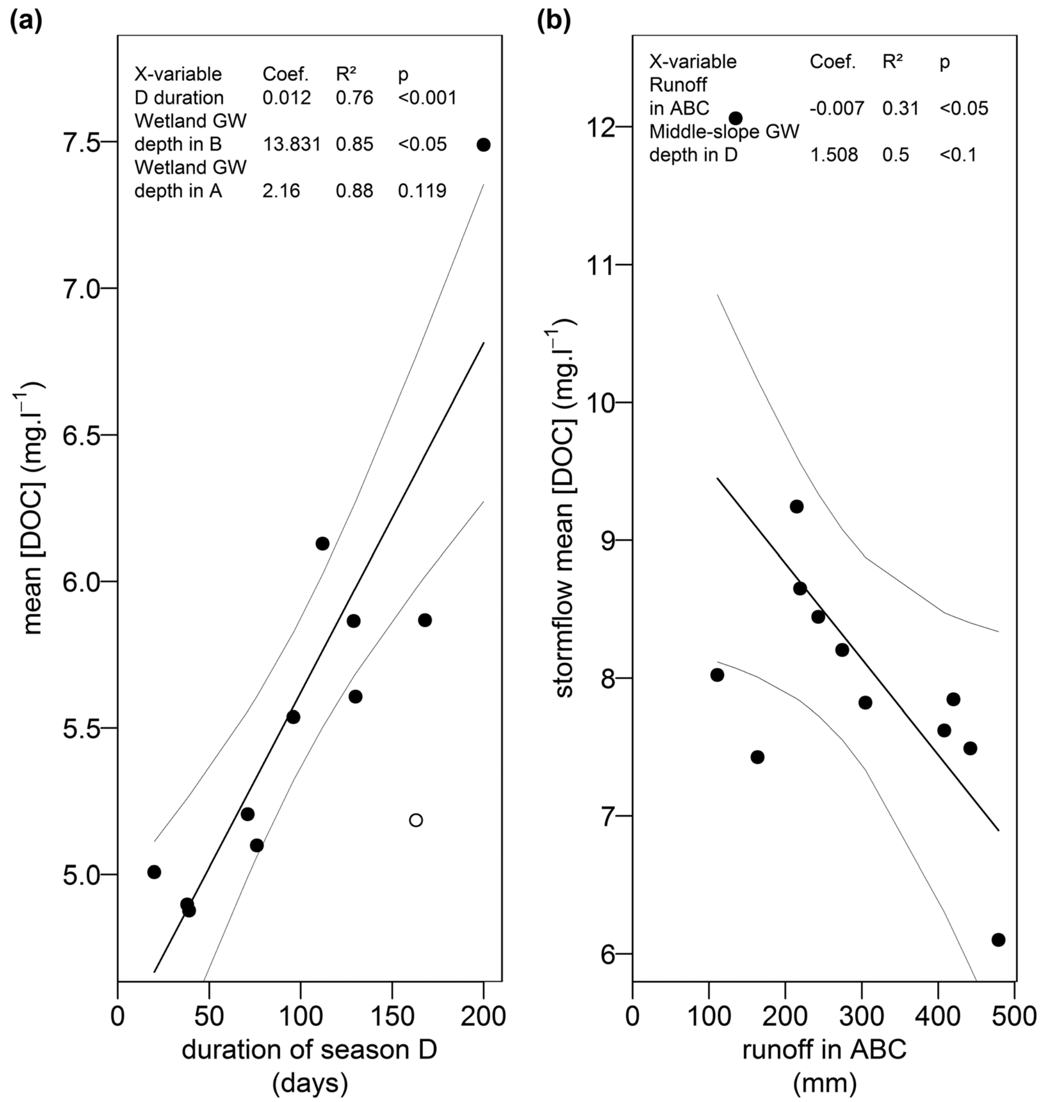

Figure 7. (a) Simple linear regression (SLR) between duration of season D and mean annual DOC concentration (n = 11). The unfilled circle represents values obtained in water year 2005–2006, which were not included in SLR and MLR due to a lack of season A that year. (b) Simple linear regression between runoff in seasons ABC and mean annual DOC concentration during storm events (n = 12). Results for the forward stepwise regression are detailed at the top of the graphs. Thin lines represent the 95% confidence interval for each SLR. D: drought; A: rewetting; B: high flow; C: recession; DOC: dissolved organic carbon; GW: groundwater table.

information Figure S4). Duration of season D and groundwater depth in the wetland domain in seasons A and B, which were three independent variables ($|r| < 0.53$ and $p > 0.1$), explained 76, 9, and 3%, respectively, of the variance in annual mean DOC concentrations ($r^2 = 0.88$, $p < 0.001$; Figure 7a). Runoff in the wet period (i.e., ABC) and groundwater depth in the middle-slope domain in season D explained 31 and 19%, respectively, of the variance in stormflow mean DOC concentrations ($r^2 = 0.5$, $p < 0.05$; Figure 7b). Groundwater depth in upland soils in season C, base flow mean discharge in season B, and groundwater depth in the wetland domain in season D explained 42, 31, and 15%, respectively, of the variance in base flow mean DOC concentrations ($r = 0.88$, $p < 0.01$; supporting information Figure S4).

4. Discussion

4.1. Linkage Between Mobilization of Limited and Unlimited DOC Sources and Stream DOC Dynamics

Previous studies suggest that DOM transferred to the stream originates from different terrestrial sources that derived either from different production mechanisms or from different locations. Then, microbial-

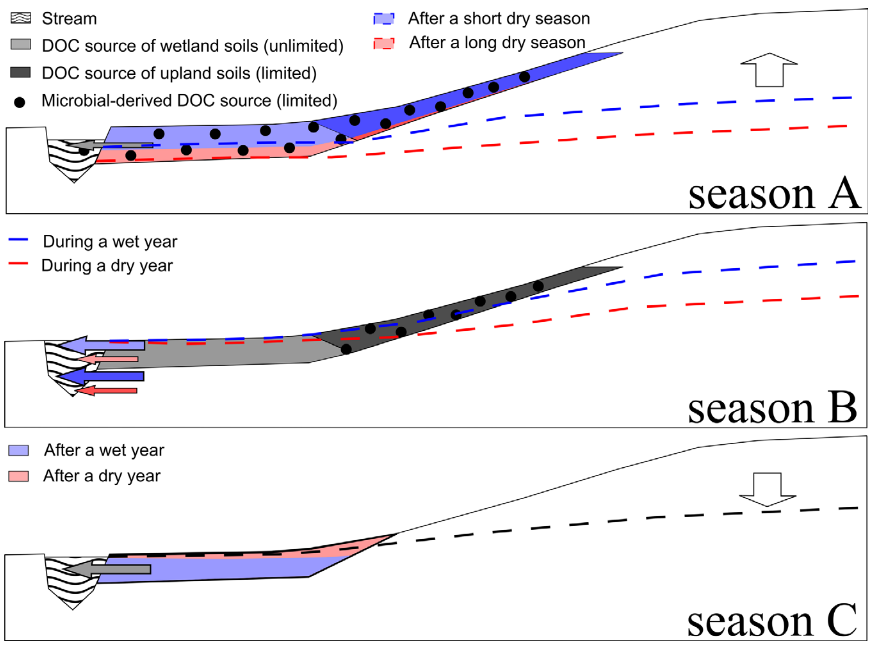

Figure 8. Conceptual diagram of the mobilization of dissolved organic carbon (DOC) pools during the water year. White arrows show groundwater dynamics. Light and dark arrows show the main DOC transfer of riparian-originated and hillslope-originated DOC, respectively, during the water year. The interannual differences are shown in blue and red.

derived and upland DOC sources are depleted after rewetting of the wetland and upland domains, respectively, while a quasi-infinite riparian DOC source is mobilized throughout the water year [*Lambert et al.*, 2013; *Morel et al.*, 2009; *Sanderman et al.*, 2009]. The seasonal dynamics of daily stream DOC concentrations reported over 13 water years in this study are consistent with this assessment.

The rapid decrease in stormflow and base flow stream DOC concentrations observed each year in season A followed by a rise in groundwater in the uppermost horizon of wetland soils confirmed the existence of an initial supply-limited DOC pool. *Mehring et al.* [2013] reported similar results in the Suwanee River Basin and suggested that the increase in groundwater level (i.e., decrease in groundwater depth) could rapidly flush a highly labile DOC pool with a low density of aromatic moieties. *Lambert et al.* [2013] also identified from specific ultraviolet absorbance (SUVA) measurements in wetland soils of the Kervidy-Naizin watershed that the DOC quickly flushed at the beginning of the water year was poorly aromatic. Therefore, they suggested that this pool could have been built up during the dry season from microbial biomass decayed due to drought, according to the results of *Christ and David* [1996]. However, this first increase in poorly aromatic DOM could also be due to products of SOM decomposition-mineralization occurring during wet-dry cycles [*Chow et al.*, 2006], or to previously sequestered carbon made available by soil-structure disruption caused by wet-dry cycles [*Lundquist et al.*, 1999]. Since the riparian margins of the Kervidy-Naizin watershed are mostly tree-filled and these areas only are connected to the stream when watershed soils are rewetted, another explanation could be a DOC input from leaf litter accumulated in the streambed and on stream banks, as reported for forested watersheds [e.g., *Singh et al.*, 2014]. The increase in both stormflow and base flow stream DOC concentrations observed between the end of season A and beginning of season B (Figure 5a) corresponds to transfer of an upland DOC source as a consequence of increased groundwater level in upland soils that connect it to the stream. The continuous decrease in concentrations for both flowtypes during season B confirms the limited supply of this upland DOC source, as demonstrated by *Lambert et al.* [2013, 2014]. However, the production mechanisms of DOM transferred from the arable upland soils remain largely unknown. The DOM characterization from SUVA and molecular biomarkers suggests that the DOM preferentially mobilized from Kervidy-Naizin upland soils would have a composition poorly aromatic and mostly microbial-derived [*Jeanneau et al.*, 2014; *Lambert et al.*, 2013]. Although these results are consistent with findings from larger-scale studies on stream DOM composition in agricultural watersheds [e.g., *Wilson and Xenopoulos*, 2009], further investigations on the composition and the kinetics of this DOM transferred from cultivated upland soils are needed. This study does not distinguish the processes involved in the production of DOM within watershed soils, but our findings suggest that longer dry season increases the DOC pools, by affecting one or several of these processes (Figure 8, season A).

Furthermore, higher decrease in DOC concentrations for stormflow compared to base flow (Figure 5a) does not necessarily imply a quicker depletion or a more limited supply of the DOC sources connected to the stream during storm events. The DOC sources preferentially mobilized during storm events (i.e., organomineral soil horizon) were more concentrated than the DOC sources mobilized in base flow (i.e., mineral soil horizons) [*Lambert et al*., 2011; *Morel et al*., 2009]. A similar rate of DOC depletion in both DOC sources can lead to the dynamics we observed (Figure 5a). Further research is required to confirm this assumption. Our findings so far emphasize that this export and depletion of DOC pools increases with runoff in wetter years (Figure 8, season B).

The convergence of stormflow and base flow concentrations during each season B and the decreasing base flow concentrations toward the same value of ca. 2–3 mg C L^{-1} are two observations supporting the existence of two different DOC sources mobilized in season B. After depletion of the upland DOC as detailed above, the wetland domain acts as a unique source of DOC, more stable and chemically recalcitrant [*Lambert et al*., 2013; *Sanderman et al*., 2009]. Since the connection between riparian wetland soils and the stream lasts from season A to the end of the water year, this source appears as quasi-infinite, as estimated by *Morel et al*. [2009]. Our findings suggest that this DOC pool will be more depleted after wetter seasons A and B than in dryer years (Figure 8, season C).

The conceptual model validated with 13 years of data seems reliable for describing consistent intra-annual patterns of stream DOC concentrations for small, shallow-groundwater watersheds in which hydrological behavior is dominated by seasonal dynamics of groundwater level along the hillslope. Further works in this watershed and in watersheds with similar functioning are required to test and refine this model.

4.2. Seasonal Factors Controlling Annual Stream DOC Exports

Despite a consistent intra-annual pattern of stream DOC concentrations controlled by DOC source characteristics and groundwater dynamics, DOC exports (fluxes and concentrations) remained variable from year-to-year and were assumed to be controlled by hydroclimatic variables. This study showed that seasonal drought conditions have a positive effect on mean annual DOC concentrations whereas rainfall during seasons A and B has a negative effect. Still, drought-related factors appear to be more important based on the regression analyses.

Annual DOC flux averaged 1766 $\pm$ 931 kg C km^{-2} yr^{-1}, which lies within the range of 770–10,340 kg C km^{-2} yr^{-1} reported by *Hope et al*. [1997] for 85 British rivers during 1993. The large interannual variability observed here is common for small upland watersheds, as demonstrated by *Alvarez-Cobelas et al*. [2012] when comparing DOC fluxes for a wide range of watershed sizes. Our study demonstrates that runoff is the primary driver of DOC flux in watersheds and thus confirmed many previous studies [e.g., *Mulholland*, 2003; *Perdrial et al*., 2014; *Royer and David*, 2005]. The lack of relevant control from other hydroclimatic variables is consistent with results of *Worrall and Burt* [2008], who showed that extreme temperatures did not significantly influence DOC flux. The high dependence of DOC fluxes on water fluxes in a single watershed emphasizes that a given watershed cannot be characterized simply by a specific DOC flux. Several years of data that encompass variations in water fluxes seem necessary to properly evaluate the actual DOC export capacity of a watershed. Without such a record period, the annual mean DOC concentration, which appears more stable for interannual considerations, is a reliable characteristic to describe the DOC export capacity of a watershed.

Annual flow-weighted mean DOC concentration calculated over 13 water years for the Kervidy-Naizin watershed (5.5 $\pm$ 0.7 mg C L^{-1}) lies in the range of 3.4–10.6 mg C L^{-1} reported by *Eimers et al*. [2008] for seven forested watersheds located at the southern limit of the Boreal ecozone. However, it is greater than the 3.1–3.9 mg C L^{-1} range reported by *Royer and David* [2005] for streams draining agricultural watersheds in Illinois, U.S., probably because these watersheds have few wetlands and few soils with high SOM contents [*Aitkenhead et al*., 1999; *Wohlfart et al*., 2012]. This study demonstrated that among hydroclimatic variables, seasonal drought conditions mainly increased annual mean DOC concentrations, while runoff in seasons A and B decreased them, regardless of the flow-type considered.

The control of mean annual DOC concentrations by antecedent seasonal drought supports previous findings. Although performed in ecosystems as different as blackwater rivers in the Suwannee River basin, U.S.

[*Mehring et al*., 2013] and Estonian rivers [*Parn and Mander*, 2012], studies have shown that longer antecedent drought led to higher stream DOC concentrations. The present study demonstrated that in addition to the length of the dry season, the magnitude of the groundwater drawdown controlled mean annual DOC concentrations. Since both variables impact all watershed soils, these results suggest that an increase in the volume of unsaturated soils in the watershed and an increase in duration of these unsaturated conditions increase production and accumulation of DOC within soils, as stated in the conceptual model. Therefore, as each DOC source progressively connects to the stream, a higher amount of previously accumulated solutes can be flushed into the stream during wet seasons. Hence, as indicated for stream DOC dynamics at the event scale [*Burns*, 2005], the DOC accumulation that occurs along with DOC production in unsaturated soils seems critical for studying stream DOC concentrations at the annual scale. These findings obtained in a temperate watershed are similar to those of *Mehring et al*. [2013] and *Parn and Mander* [2012] and of studies performed in a boreal ecosystem [*Agren et al*., 2010; *Haei et al*., 2010], where longer and colder winters result in higher soil and stream DOC concentrations during the subsequent snowmelt. Although production processes can differ between these ecosystems, the duration of seasons with low water flows and DOC exports seems a critical factor controlling mean stream DOC concentrations recorded during subsequent seasons of high water flow.

Greater connection between soils and higher base flow discharges during wet seasons can offset effects of the antecedent dry season by decreasing mean annual DOC concentration. Although this agrees with previous studies showing stream discharge or antecedent water export to be factors negatively controlling mean DOC concentrations [*Agren et al*., 2010; *Mehring et al*., 2013], it challenges the concept that concentrations increase when connectivity between sources and the stream increases [*Laudon et al*., 2011]. Three mechanisms could explain the decrease in mean DOC concentrations despite high groundwater levels, high base flow discharges and high water export: (i) more efficient flushing in wet years than dry years and less time to rebuild DOC stores between events [*Inamdar et al*., 2008; *Turgeon and Courchesne*, 2008], (ii) shorter water transit times due to higher hydraulic gradients during wet years that decrease diffusion of DOC between micro and macropores in the saturated topsoil of the wetland domain [*Kalbitz et al*., 2000], and (iii) an increase in overland flow or a change in flow partitioning within the soil profile in the saturated downslope area that dilutes streamflow more in wet years than dry years [*Laudon et al*., 2011].

In summary, two antagonistic processes determined by groundwater dynamics control the annual pattern of stream DOC concentrations during the hydrological year: (i) DOC production-accumulation in soil during the dry season and (ii) dilution-depletion of these sources when DOC is transferred to the stream during wet seasons. These results seem relevant for watersheds in which the complex interactions between subsurface flow and groundwater dynamics dominate hydrological processes, which is a common feature shared by many well-vegetated temperate watersheds developed on fractured and weathered bedrocks [e.g., *Beven*, 2006; *Gabrielli et al*., 2012; *van Verseveld et al*., 2009].

4.3. Implications for the Study of Interannual Variations in Stream DOC Concentrations

Similar results reported for contrasting watersheds [*Agren et al*., 2010; *Mehring et al*., 2013] and in this study highlight the ability of wet seasons to mitigate, through dilution-depletion, the production-accumulation of DOC occurring in soils during seasons with reduced water export due to dry or freezing conditions. Thus, interannual variations in the antagonistic processes that occur within a year are controlled by hydroclimatic variables, with effects that can be approximated from groundwater level dynamics. Owing to these processes, high interannual variability in dry and wet season features led to low interannual variability in stream DOC concentrations in the Kervidy-Naizin watershed. For instance, the combination of extreme drying conditions in summer 2003 with relatively high runoff in water year 2003–2004 led to smaller annual mean concentrations than in 2011–2012, when the long dry season in 2011 was combined with low water runoff. Superimposed on the presence of a quasi-infinite DOC source in the wetland domain [*Morel et al*., 2009], these antagonistic processes could explain the year-to-year resilience of the response of stream DOC to climatic variations reported for this watershed. However, computer simulations of this watershed by *Salmon-Monviola et al*. [2013], based on future climate projections, predicted that spring and summer groundwater recharge and annual discharge will decrease between 1961 and 2099. Combined with these predictions, our results may indicate that mean annual DOC concentrations will increase in the future.

Long-term changes in temperature, hydrology, acid deposition, land use, nitrogen, and CO_2 enrichment have been suggested as possible drivers of increasing trends in DOC concentrations reported in freshwaters over the last three decades in the Northern Hemisphere [*Erlandsson et al*., 2008; *Evans et al*., 2005; *Freeman et al*., 2001; *Jarde et al*., 2007]. However, many rivers and lakes show no significant increasing trends or even show significant decreasing trends [*Monteith et al*., 2007; *Worrall and Burt*, 2007], and divergent trends are reported for nearby watersheds. Results of this study, along with those of previous studies showing long-term trends in stream DOC concentrations [*Erlandsson et al*., 2008; *Mehring et al*., 2013; *Parn and Mander*, 2012], highlight that intra-annual antagonistic processes and an unlimited riparian DOC source can mitigate or even obscure global changes. Noticeably, changes in environmental conditions could also alter production and chemistry of DOC in riparian areas which could result in a change in the baseline DOC concentrations. The specific results reported here highlight the need to consider seasonal hydroclimatic changes within years and from year-to-year by using proxies that describe watershed functioning.

5. Conclusions

Antagonistic mechanisms of production-accumulation and dilution-depletion in the DOC pools of watershed soils limit the solute dynamics [*Burns*, 2005]. As a driver of the connection between the stream and DOC sources, the groundwater dynamics in response to climatic factors can control both these mechanisms.

From the study of interannual changes in seasonal hydroclimate variables and stream DOC dynamics over 13 years of daily monitoring in a small, shallow groundwater-dominated watershed, we showed that (i) intra-annual patterns are similar across years and are controlled by DOC source characteristics and groundwater dynamics and (ii) dry season characteristics determine the variation of mean annual DOC concentrations while annual runoff determines the annual flux.

These findings highlight the relevance of considering the seasonal dynamics of hydrological connectivity within the watershed (e.g., in this case via groundwater levels) when studying the annual DOC transfers. Finally, intra-annual antagonistic processes combined with an unlimited DOC supply in riparian wetland soils could explain the mitigated response of stream DOC concentrations to global changes and climatic variations reported in some watersheds.

The model proposed from our findings call for further investigations using source tracking tools (i.e., fluorescence, stable isotopes, and molecular biomarkers) to characterize the temporal dynamics of DOM sources.

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